STUDIES UPON THE HYDROGENATION OF KANSAS COALS

by

JOHN F NIENSTEDT

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INTRODUCTION

Coal as a future source for our motor fuel is a possibility. In this country we have an abundant supply of crude oil at the present time and we can not see any immediate exhaustion of this supply, so we have not in this country done much work on securing motor fuel from coal. We have, though, in this country such an abundant available coal supply that it may be considered as a future source of motor oils.

Up to date most of the work on Hydrogenation of Coal has been done in Europe. The reason for this is that Europe does not have an abundant supply of crude oil, and therefore they have been looking to other sources for their future motor fuels. The countries of Europe which have done the most along this line are Germany, England, France, and Italy.

Dr. Friedrick Bergius of Germany has been working on the transformation of coal into oil by means of hydrogen since 1913. A plant was built in 1926 for the application of his process at Mannheim Rheinu, Germany, and it is running on a commercial basis. Dr. Franz Fisher in Germany and General Patard and M. Audibert in France have carried on considerable research on synthesis of motor fuels. J.

I. Graham of England has also done research along this line.

A study of the hydrogenation of coal is practically a study of the work that has been done by Dr. Bergius. Three different lines of work, differing in principle, have been followed in solving the problem of obtaining a substitute for natural oil from coal.

The oldest is called low temperature distillation. This process no doubt will play an important role in making a special kind of coke and recovering a certain amount of low temperature tar. In this process oil would just be a by-product.

The second principle is the synthetic manufacture of oils from coal products. The basis of chemical oil synthesis is the building up of hydrocarbons from their chemical elements. A direct synthesis of hydrocarbons from carbon and hydrogen is possible but of no interest from the industrial stand point.

The third principle is the direct liquefaction of coal by means of hydrogenation. In 1913 in Hanover, Germany, the direct addition of hydrogen to coal was first carried out by Dr. Bergius. They called this process the coal liquefaction process. Invention of coal-liquefaction was not accidental, but was the result of a long study of the chemical nature of coal. It was found that by using high

temperature and pressure the hydrogen could be made to unite with coal without the addition of catalysts.

Great difficulties arose as soon as larger quantities were used for the reaction. A solid hydrogen oil material was no longer produced, but instead a cokey substance. The reason for this was found to lie in the fact that the hydrogenation reaction produced a large amount of heat, which could be led off only with difficulty from the system of gases and solid material. This new difficulty from the gases was overcome by carrying out the reaction in the presence of a liquid medium such as coal oil. Hydrogenation began at relatively low temperatures. It is treated for a few hours at 300°-350° C and then the temperature ran higher. The product became liquid at 420° C. Therefore the coal liquefaction process really consists of two different processes, the first, hydrogen addition, the second, the splitting up of large molecules into smaller ones while new hydrogen is being added. The higher the temperature, the more the larger molecules are broken up into smaller ones.

Typical representatives of the aliphatic, aromatic, and hydro-aromatic series are found in the coal liquefaction products, except the unsaturated compounds which can not be formed in the presence of high pressure hydrogen. Besides these chemical compounds those of phenolic char-

acter, chiefly kresol and ammonia, are among the products.

Almost all lignites have a greater reaction velocity and liquify more completely than bituminous.

The economics of the process is of course very important. The consumption of raw material and energy, wages and depreciation, and cost on the one hand, and the value of the finished product on the other, are factors to be considered. Raw materials are coal or lignite and hydrogen. The cost of the coal or lignite is small. The production of hydrogen is the fundamental point in the economy of the process. If coal-liquefaction had to depend on the usual hydrogen-manufacturing processes for its supply, it would be difficult to make oil in competition with the natural product. Hydrogenation does not require a pure hydrogen; therefore, it can use hydrogen secured by a different process. It consists in heating the gaseous reaction products in the presence of steam, whereby the needed hydrogen is regenerated.

The most important processes of producing oil from coal are in the hands of the German Chemical Trust, the J. G. Farbenindustrie, and of the Ruhr Coal Syndicate. They have lately proven to be economical.

The oily parts which are won by the Bergius process must be distilled carefully by methods which are similar to those used in the oil industry in order to get market re-

sults. For heating and power generating purposes, to hold up the process of hydrogenating one ton of coal, 800 pounds of coals are required. Therefore altogether 2800 lbs. of coal are necessary to produce about 1000 lbs. of valuable oil and some ammonia. These figures apply to coal of good quality.

A plant which produces 50,000 tons of artificial coal oil per year will cost about $8,000,000. The cost of producing this oil is figuring in the prices of coal, power, depreciation of plant, labor on the 1927 market. Figuring what the product was worth on the 1927 German market the price of oil could slump 60-70% without the economy of this process being endangered. The prices of oil in Germany are more stable than in our country because they do not have the great producing oil fields being brought in, such as the East Texas field.

Lately experiments have been conducted with the action of catalysts upon hydrogenation of coals with the view of reducing the reaction time, lowering the optimum temperature, and decreasing the pressure of H_2. The rate of hydrogenation is not only increased by true hydrogenating catalysts such as nickel, cobalt, etc., but also by those which are used for cracking the heavier oils such as $AlCl_3$, $FeCl_3$, and $ZnCl_2$. Hydrogenating catalysts accelerate the decomposition of organic molecules at a high temperature,

while the cracking catalysts favor the hydrogenation of aromatic compounds, provided the optimum temperature is not exceeded.

$NiCl_2$ is best fitted for hydrogenating most lignites. CuCl is less influential than $NiCl_2$. The absorption of H_2 is lower, the quality of the oil is poorer, more cracking occurs. ZnO+KOH mixture is inferior to CuCl but is better than Fe_2O_3 used alone. $CaCl_2$ has no effect upon the hydrogenation of coal. The best catalysts have been found to be Fe_2O_3, $ZnCl_2$, ZnO, $NiCl_2$, NiO, $CoCl_2$, CuCl. These catalysts do not allow the temperature or pressure to be lowered without affecting the yield of products but influence (1) the intensity of the reaction (2) rate of decomposition of the coal mols and (3) rate of hydrogenation only secondly. All these experiments were made without a previous addition of oils. Oils hasten and favor hydrogenation and increase the yield of gasoline.

There has been lately research carried on in this country on the Hydrogenation of oils. This has been carried on by the Standard Oil Company and also by the Sinclair Oil Company in East Chicago.

My work in undertaking the Hydrogenation of Kansas Coals was to analyse the Kansas coal available, to investigate the theory and mechanics of the liquefaction of the coal, and to compare the Kansas coals to those of Europe

as materials for hydrogenation, and to apply by experimental work the principles of Hydrogenation of coal.

STRATIGRAPHY FOR KANSAS COAL MEASURES

Reference: University Geoligical Survey of Kansas- Erasmus Hayworth.

The Stratigraphy of the Kansas coal measures may be divided into two parts with many sub-parts under part two.

1. Mississippian or Subcarboniferous:
   This layer only covers about forty-five square miles in the southeast corner of the state.
2. The Coal Measures:
   a. Cherokee Shales.
      This covers a large area of Kansas. It is found in Cherokee, Crawford, Labette, and a part of Bourbon counties. This shale is known to exist in counties farther west because it has been found on the bits of oil drilling outfits. This coal is a good bituminous coal.
   b. Labette Shales.
      Between the Labette and Cherokee shales there is a layer of limestone. The Labette shale is above the Cherokee shale. This layer furnishes practically no coal.
   c. Pleasanton Shales.

On top of the Labette shales is a layer of limestone (Pawnee) and then on top of this limestone is the Pleasanton shale. The lower pleasanton shales contain considerable coal, but the upper shales do not.

d. Thayer Shales.

Above the Pleasanton shales there are the Erie limestone and then directly above this is the Thayer shales. This yields quite a bit of coal.

e. Lane Shales.

Above the Thayer shales. They carry practically no coal.

f. Lawrence shales.

These carry a fairly good coal. Mines are in Franklin and Douglas counties.

g. Lecompton Shales.

Practically no coal.

h. Severy shales.

No coal.

i. Osage Shales.

A fairly good coal shale. Mines located around Osage City and Burlingame.

Most of the marketable coal in Kansas comes from the Cherokee shales. It is the best coal although it is found

at the greatest depth of any of the known coals. The coal that was used in hydrogenation came from the Cherokee shales. The Thayer and Osage shales also furnish some coal but the mines in those shales only furnish local markets. There are practically no coal in the Labette, Lane, or Bevery shales. Those shales vary in width from 25 feet to 500 feet.

PROXIMATE ANALYSIS OF KANSAS COALS

References: Analysis of delivered coal, State of Kansas Technical paper 445-
Bureau of Mines.

Mines	Moisture %	Volatile Matter	Fixed Carbon	Ash	Sulfur
Atchison-Cherokee	7.0	33.4	42.5	13.1	3.6
Cherokee County Mineral	4.6	32.7	38.9	13.4	5.1
Carbon Nos.4 & 5	5.4	32.5	55.1	12.4	5.1
French No. 1	2.9	34.6	56.5	8.9	3.7
Do (Cherokee Co.)	3.7	35.9	36.1	8.0	3.0
Souther No. 9	2.5	34.7	52.5	12.8	5.8
Atwood Bros. No.2	3.6	34.9	55.4	11.7	5.6
Do (South End)	2.5	35.3	56.4	8.3	4.1
Hamilton No. 9	3.2	33.4	51.6	14.3	2.7
Western No. 10	5.0	34.4	51.9	13.7	4.5
Western No. 15	4.1	33.3	51.3	15.4	4.8
Cherokee Pittsburg No. 11	5.3	35.3	50.2	14.5	5.4
Lone Star	3.3	37.4	55.0	7.6	3.6
Western No. 11	4.2	32.6	48.7	18.7	6.5
Carr	3.8	39.0	45.3	17.7	5.1
Do (Leavenworth Co.)	9.4	40.8	44.2	15.0	5.0
Pleasanton (State line)	7.7	34.0	45.8	20.2	3.9

FORMATION OF COAL

Reference: Coal- H. S. Moore and Geology- Salisbury.

It is almost universally agreed that all the varieties of coal originated from vegetal matter. Some geologists contend that the coal beds are where the vegetation grew and fell. Other geologists contend that it accumulated as a result of the transportation of the vegetable matter by water. The purity of the coal seems to prove that the vegetation grew where the coal is. The vegetation grew in swamps or in boggy land. The water which would cover the vegetation when it fell preserved it and kept it from decaying as it does on land.

In air the carbon and hydrogen of the wood unite with oxygen of the air, forming carbon dioxide and water. Under water the atmospheric oxygen is excluded and the elements of the wood are thought to unite with one another to a larger extent. This produces marsh gas (CH_4) as an example. If carbon dioxide is also formed, and it is thought that it is, the oxygen is exhausted twice as fast as the carbon, and the result is a larger amount of carbon remaining. For example-- Cellulose ($C_{72}H_{120}O_{60}$) and peat ($C_{62}H_{72}O_{24}$) and bituminous coal ($C_{24}H_{22}O_2$). This shows how

coal might be formed by the illustration given above.

HYDROGENATION

In 1913 in Hanover, Germany, the first direct addition of Hydrogen to coal was carried out by Dr. Bergius. In these first experiments a "coksy substance" was formed. This difficulty was overcome by carrying out the reaction in the presence of a liquid medium (coal oil). They found that if too high temperatures were reached the substances coked regardless of the "coal oil".

According to Dr. Bergius, in his paper read before the International Conference on Bituminous Coal, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, hydrogenation of coal begins at relatively low temperatures. Treated for a few hours at 300-350° C, the product is still solid, but it is transformed into a sort of pitch with a high melting point; this will become liquid if treatment is continued at a temperature of 425° C. The pressure should range from about 150 atmospheres to about 200 atmospheres or a pressure of from 2200 to 3000 pounds per square inch.

Dr. Bergius stated that no special coals are required. All coals can be hydrogenated except anthracites. Lignites as well as bituminous can be hydrogenated.

Mechanical equipment was quite a problem. Methods had to be developed for carrying thru the coal liquefaction in

a continuous process. The coal was ground very fine and run thru 60 mesh sieves. The coal was then added to heavy oil of a previous run and made into a pasty mass. This was then run into the reaction vessel. Hydrogen was also pumped into the reaction vessel and the contents stirred with a stirring rod. The reaction vessel was heated from the inside. The vessel had to be heated from the inside because it would not hold the pressure if the vessel was heated up as hot as it would have to be on the outside to get the required heat on the inside. In this process catalysts may or may not be used. If they are used it is to take out the sulfur or other impurities. The metal oxides from the fourth to eighth groups are usually used for catalysts.

TABLE I

Sample yields of the Bergius Process.

Reference: Automotive Industries for November 25, 1926, page 806.

(1) Basis: 1000 pounds of coal liquified under pressure

200 pounds of middle fraction products

150 pounds of marketable gasoline

Residue:

60 pounds of lubricating oil

80 pounds of fuel oil

(2) Basis: 1 short ton of coal

443 kilograms of oil

5 kilograms of ammonia

210 kilograms of gas

300 kilograms of residue which contains:

80 kilograms of oil

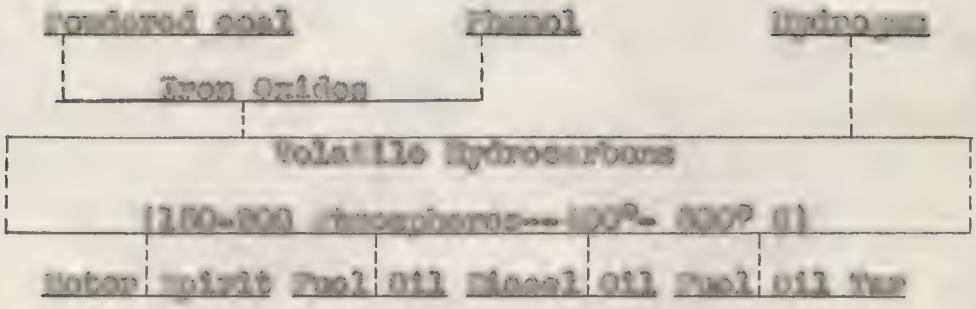
240 kilograms of coke

25 kilograms of gas

Table II

Bergius Process

Flow Sheet (Chemical)



REACTIONS

1. Absorption of hydrogen

   Unsaturated-Hydrocarbon+Hydrogen → High Molecular Weight Molecules

2. Elimination of impurities with iron

3. Formation of low boiling hydrocarbon

   Liquid Phase+Hydrogen → Volatile Hydrocarbons

(1) Kansas Coal--

An ordinary grade of Kansas coal was used for this work. The coal was crushed to 60 mesh grade and then analyzed.

It contained: 1.625% moisture
16.4 % ash
36.6 % volatile matter
3 to 4% sulfur
51 to 52% fixed carbon

(2) Hydrogen Gas--

The hydrogen used was the hydrogen which was obtained from the Kansas City Oxygen Co., Kansas City, Mo. The hydrogen was obtained in steel drums.

(3) Liquid Media Used--

In part of the tests a liquid media was used. When a media was used it was to prevent over-heating. Two different medias were used:

(a) Road oils
(b) Waste lubricating oil from the Industrial laboratory.

(4) Catalysts--

Tests were made both with and without catalysts. When catalysts were used such catalysts as iron oxide, nickel chloride,

barium carbonate or zinc oxide were used.

HYDROGENATION APPARATUS USED IN THE LABORATORY

This apparatus may be divided into three classes:

(1) Apparatus used in preparing of coal sample and charging the bomb.

(2) Hydrogenation apparatus.

(3) Apparatus used in testing the products.

Preparation of coal samples

(a) Crushing apparatus consisted of the Braun pulverizer.

(b) Screening apparatus consisted of the Tyler Standard Sieves 20, 40, 60 mesh screens.

(c) In the preparing of the coal charge a platform scale was used in weighing out the coal and the amount of liquid media wanted if any was used and then they were mixed in a pan.

(d) In charging the bomb with the coal the coal was poured into the bomb by hand.

(e) Charging the hydrogen was a different process. Extra strong wrought steel pipe threaded with 3/8" pipe threads was used. One end of the pipe was screwed into the valve on the bomb and the other end screwed into the hydrogen tank by means of a reducing coupling 1/2" to 3/8".

Hydrogenation Equipment

(a) Agitation machinery. (Figure I).
It consists of a motor driven eccentric on shaft and a jig and cradle support with center bearing roll and bomb supports and clamps. It was driven by a 220 volt-1725 rpm A. C. motor with a belt drive.

(b) Two "illium" steel bombs 12½" long and 6" in diameter. The bombs had an internal area of 331 cubic inches or approximately one gallon. They weigh 39½ alone and 58 pounds when assembled.

(c) The bomb fittings consisted of two nipples consisting of extra strong wrought steel pipe 3" long. One pipe lead to the gauge and the other to the valve.

(d) Control units high-pressure fittings
(1) Edward 3/8" threading high-pressure valve-Y-Style. Later needle valves were used.
(2) 3000 pounds per square inch capacity pressure gauges.

(e) Heater units: Type Y 1650 G. E. Calrod strip Heaters. 220 volts and 250 watts rating. Four strip heaters 12" long and 1½" wide. Asbestos was used for insulation around the strip heaters and a metal case around this about 14½" in di-

meter and 12½" tall.

(f) A pyrometer was used to record the temperature. (Figure 2).

(1) Leeds and Northrup resistance type was used. It consisted of:

(1) Platinum Pyrometer 202075 (Bomb I)

(2) Platinum Pyrometer 202074 (Bomb II)

(3) 10 point rotary switch

(4) L & N resistance thermometer indicator-galvonometer.

(5) Two resistance blocks

(6) Wiring contacts

(2) Thermocouple pyrometer by the Brown Instrument Company

(3) Checking instrument was a 400° C thermometer. (Figure 2 will show this pyrometer equipment.)

Testing Equipment consisted of:

(a) Crucibles, tongs, burners, etc. for determining the "Proximate Analysis of Coal".

(b) Gas holding and testing apparatus.

(c) Distilling apparatus consisted of distilling flasks, condensers, etc.

(d) Apparatus to test the specific gravity of product such as balances, hydrometers, etc.

(e) Optical systems such as reflectometer and
microscope.

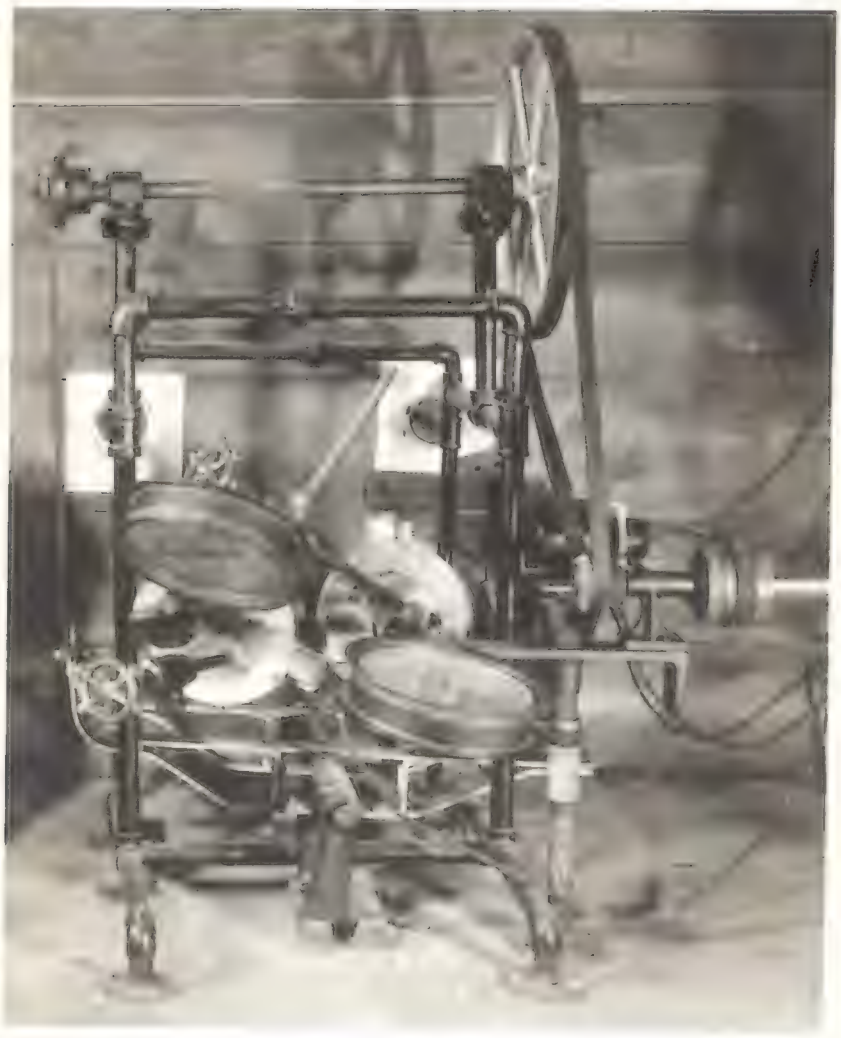


Figure 1. Agitation Machinery.

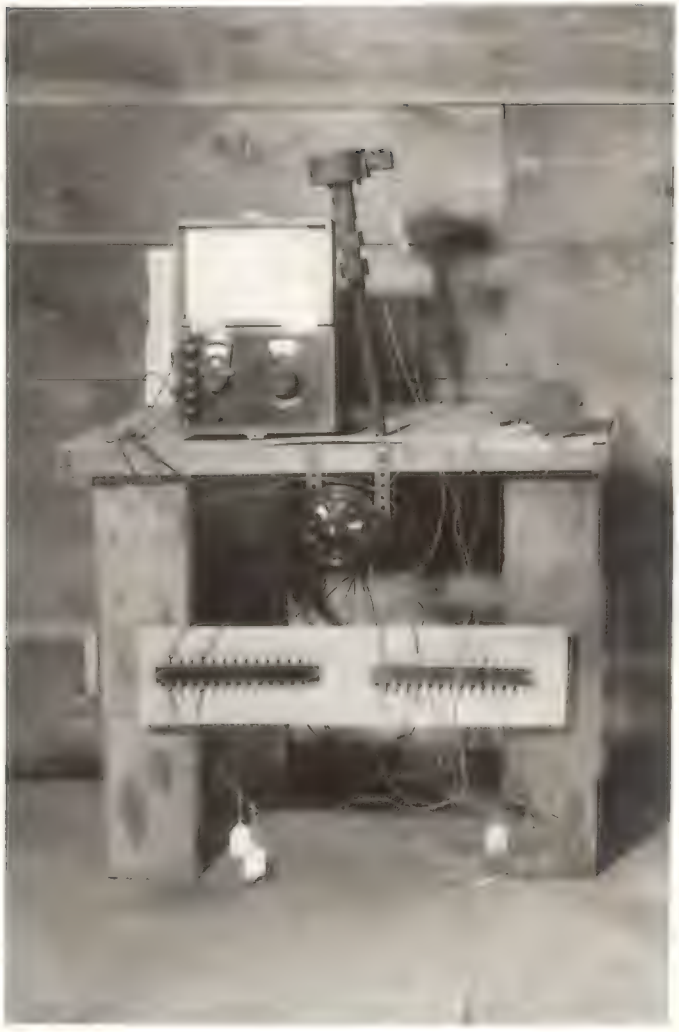


Figure 2. Pyrometer equipment.

PRELIMINARY EXPERIMENTS

An initial test was made on the hydrogenation apparatus to test the heater units. This experiment was carried out by steam expansion.

About ½ gallon of water was placed in bomb 1. A steam resistant gasket was used with the plug to prevent leakage. The bomb was fixed as it would be for a hydrogenation test, and a thermocouple was used to record the temperature. When the temperature was up around 400° F, the gasket leaked.

DATA

Time	Temperature °F	Pressure lbs. per sq. in.
9:30 A. M.	80°	00 Lbs.
10:00	250°	00 "
10:30	360°	240 "
11:30	480°	650 "
12:00 (Noon)	520°	150 "
1:00 P. M.	260°	
4:00 P. M.	100°	

TESTS WITH DIFFERENT CATALYSTS

1. Copper Oxalate Stellite and Glycerine and Litharge Mixtures.

In charging the bombs for the test there was approximately one pound of coal mixed with enough coal oil to make a paste. This amount was placed in each bomb. Hydrogen was then run into the coal bomb to the desired starting pressure.

The starting temperature was 28° C. and the barometric pressure was 73.0 cm.

BOMB I			BOMB II		
Time	Temperature	Pressure	Time	Temperature	Pressure
3:20	28° C.	530 #sq"	3:20	28° C.	560#
4:00	42°	625	4:00	52°	610
4:25	94°	670	4:25	116°	720
4:45	139°	670	4:45	150°	750
5:00	143°	620	5:00	158°	375
5:15	146°	540	5:15	159°	260
5:30	141°	490	5:30	138°	130

The temperature rise was about one degree per minute. bomb I started to leak at about 4:45 o'clock when it had attained a pressure of 670 pounds and a temperature of 130° C. Bomb II started to leak at about five o'clock when it had attained a pressure of 730 pounds and a tem-

perature of 150° C.

The leakage was caused because the gaskets did not fit well enough and because the cement mixture melted. The cement mixture would have held more pressure at a lower temperature.

5. For Copper and Tin Gaskets, with Silica and Sodium Silicate and Kaolin Cements.

	BOMB I		BOMB II	
Time	Temperature	Pressure	Temperature	Pressure
9:40 A.M.	30°C	480 #/sq."	30°C	690
10:10	92	490	47	750
10:20	93	510	75	840
10:25	125	490	121	930
10:30	163	490	160	1010
10:40	199	450	190	1100
10:45	220	440	230	1140
10:50	246	430	251	1130
11:00	259	420	271	1110
11:10	279	400	287	1000
11:15	293	375	305	700
12:00	359	200	270	150
5:30 P.M.	62	0	64	

Bomb I started to leak when it had only reached a temperature of 359°C and a pressure of 420 pounds.

Bomb II did not start to leak till it had reached a

temperature of 550° and a pressure of 1140 lbs. This bomb leaked at several places. It leaked at the pipe fittings and out of the gasket. The gasket leaked because of improper seating and the melting of the cement.

3. Copper and rolled tin pipe gasket with gasket shellac.

In the tests with both bomb I and II the valves leaked and so no tests were made. The valves were reseated and a test made using the same coal sample. The valves still leaked, so they were taken to the shops to be ground, and later they were placed on the bomb and tried again. This time they leaked more than before, so it was decided to discard these valves and get some 3/8" needle valves for further tests.

CONCLUSION OF QUIET TESTS

In these tests the desired pressure was never obtained. It was not possible to find a gasket that would hold. It was desirable to find a gasket which was impervious to hydrogen which would not melt at 400° C, and which could be rolled perfectly smooth and fit perfectly tight. Most of the metals that were used for gaskets would not stand the heat. Lead and tin worked as long as the bomb was cold, but they would not stand the increased heat. Copper would stand the heat, but it would not fit perfect enough. The gasket cements that were used would not stand the heat without melting.

After each test that was made the gas in the bomb was collected, and it was found to burn with a blue hot flame. When tested with barium hydroxide they gave evidence of carbon dioxide. These gases also smelled of hydrogen sulfide.

When the inside of the bombs were opened, they were found to consist of a top layer of coke and a lower layer of oily coal residue. In the tests where this was found the raw products were coal mixed with road oil. The bombs were cleaned out by breaking the top coley layer with a steel drill and then washing the bottom layer out with some waste kerosene and compressed air. In the later

gasket test dry coal was used and did not coke as much.

The bombs fitted with plug and gasket opening did not work satisfactorily, and in further tests different set ups were used. Needle valves replaced the old valves in later work, and they were cleaned after each test. The shaker was rebuilt to cut down the speed and to do away with much of the vibration.

TEST MADE WITH PIPE APPARATUS

This apparatus consisted of:

a. 18 feet length of 3/8" extra strong wrought steel pipe.

b. 3000° per sq. inch pressure gauge put on one end of pipe.

c. Needle valve with pipe fitting to fit hydrogen tank on other end of pipe.

d. Ring stands and clamps to hold the pipe one foot above the top of the desk.

e. Two six foot lengths of pipe with saw cuts every inch to serve as a gas heater. This pipe was attached to the gas and compressed air lines with rubber tubing.

f. Clamps to hold the heaters two inches below the steel pipe.

g. Thermocouple for taking temperature.

h. Laboratory apparatus used for the other tests.

Test No. 1:

Ten grams of dry coal was placed in the pipe. Hydrogen was let in at a pressure of 900 pounds per sq. inch. In thirty minutes the pressure was 1450 lbs. At the end of one hour the pressure had risen to 1750 pounds where it remained two hours. At the end of two hours the heat was

removed. This was allowed to set overnight, and the next morning the pressure gauge read 650 pounds.

The gas in the pipe was collected over water. It burned with a hot blue flame. It left a slight scum on the water. The coal in the pipe had coked to a certain extent, otherwise no change in it was noted.

Test No. 2:

The pipe was recharged with dry coal and hydrogen was run in to a pressure of 1065 pounds. Heat was applied to this, and after one hour of heating the pressure ranged from 2100 pounds to 2200 pounds for an hour and forty-five minutes. The temperature was tested by the thermocouple and found to be from 4000-425° C. The gas was then turned off and the pipe cooled down to room temperature, and the pressure then registered 750 pounds. The gas which was collected smelled of benzene and burned with a blue hot flame. The coal in the pipe was coked considerably.

Test No. 3:

The pipe was recharged with dry coal, and nickel chloride and iron oxide were added to act as catalysts. The pipe was charged with hydrogen to a pressure of 1250 pounds. Heat was applied, and the temperature registered 400° and the pressure 2500 pounds. The pressure stayed at 2500 pounds for a time and then fell back to about 2250 pounds. It stayed at this pressure for a time. More heat was ap-

plied, and the pressure then read 2500 pounds. The temperature was about 300° C. The pressure was constant here for a while; then the pipe broke at the screw, and the gas which came out burned with a very blue flame.

Test No. 4:

The pipe broke about two feet from the end, so the broken end was sawed off and the pipe set up for another test. This time the coal was made into a paste with a little waste lubricating oil. Nickel chloride and iron oxide were added to act as catalysts. It was charged with hydrogen to a pressure of 1400 pounds at room temperature. It was heated to a temperature of about 325° C and had a pressure of 3400 pounds. This was run till the pressure had fallen back to 2500 pounds, which took about one hour. More heat was added, and the pressure was kept from 2500 pounds to 2600 pounds for two hours longer. The pipe was allowed to cool to room temperature, and the pressure was 650 pounds. The gas smelled of phenol and coal tar products. There was a dark liquid on the water over which we collected the gas. The residue in the pipe seemed to be unchanged. There was not any coking tendency on part of the residue.

Test No. 5:

Coal sample as in test No. 4 was used except that in this test zinc dust, iron oxide, antimony metal, and copper

oxide were used as catalysts. Hydrogen was run in to a pressure of 1400 pounds. The pipe was heated and held the pressure at 2200 pounds to 2400 pounds with temperature of 350°-400° C for five hours. The heat was removed, and when the pipe returned to room temperature the pressure was 625 pounds. The gas was collected, and it had a strong benzene odor.

The pipe was recharged with hydrogen to 1150 pounds. The pipe was heated to a temperature of 350° C and a pressure of 2200 for one and a half hours. The pipe broke, and the escaping gas burned with a very blue flame.

Test No. 6:

Broken part of pipe was cut off, and the pipe was recharged as before. The pipe had been weakened so much from previous trials that it broke readily again.

CONCLUSION OF PIPE TESTS

The drawbacks to the pipe tests were that the sample used was very small and it was hard to get the pipe agitated. A ten gram sample of coal was about all that could be used, and it was difficult and almost impossible to get it spread out in the pipe. It was also rather hard to get the exact temperature.

The advantages of these tests were that the desired pressures and temperatures were reached and could be held there for several hours. A temperature of 400°-500° C was obtained and a pressure of from 6000 pounds to 9000 pounds.

In these tests the gas contained a benzene gas, and the residue at times contained some coal tar derivatives. The pipe breaking prevented other tests being made. The pipe was rated to hold 14,000 pounds at room temperature. With increased temperature the tensil strength increased to about 300° F, and from there on up the tensil strength fell off considerably. At 500° C the pipe was rated to hold about 2800 pounds. The pipe always broke at the seam. Better strong seamless steel pipe could be made to work successfully.

The same apparatus was used in these tests that was used in the earlier bomb tests except that the idea used in closing the opening in the bomb was different.

In bomb I (Figure 3) a six inch length of extra strong wrought steel 1¼" pipe was screwed into the bomb and then welded around the threads. On the upper end a flat steel disc 4" in diameter was welded. It had an opening in the center the same size as the pipe. Another disc 4" in diameter was made to fit the other disc. This disc was solid and held down on to the other disc by a clamp which exerted its force on the center of the top disc. Three types of gaskets were used: (1) rolled copper, (2) asbestos, (3) combination lead and asbestos.

This idea did not work successfully because the clamp holding the top disc onto the bottom disc exerted its force in the center of it and sprung the outer edge of the disc upward. Further tests were prevented on this bomb because it had a crack in it.

In bomb II (Figure 4) an eight inch length of extra strong wrought steel 1¼" pipe was screwed and welded in the bomb. On the top end of the pipe threads were machined on. A steel screw cap was made by the Shops Department to fit these threads. The idea of this was that the pipe was long

Figure 3. Bomb I.

Figure 4. Bomb II.

enough to keep the top end of it from getting hot, and therefore red lead or glycerine and litharge could be used on the threads to prevent leakage. This idea worked successfully.

Several tests were made with bomb II.

Test No. 1:

The bomb was charged with 1 pound of dry coal. Hydrogen was then run in to a pressure of 1300 pounds at room temperature. At the end of two hours the pressure was 2500 pounds. The temperature rose at the rate of 2° per minute, and at the end of one hour it was 300° C. The pressure was kept at 2250 pounds to 2500 pounds for three hours. It was then allowed to cool to room temperature, and the pressure was then 1130 pounds. The gas was collected, and when it was tested with a flame it popped like hydrogen. The bomb was opened and examined; the residue was found to be practically unchanged except for a slight coking tendency.

Test No. 2:

The bomb was recharged with dry coal to which nickel chloride and iron oxide had been added to act as catalysts. It was charged with hydrogen to a pressure of 1250 pounds. It was then heated, and after one hour and forty-five minutes the pressure was 2650 pounds and the temperature 330° C. The pressure was kept between 2300 pounds and 2650 pounds for four hours. The bomb was then allowed to cool,

and the gas collected. The gas had a tendency to pop like hydrogen, but it also burned for a few moments with a blue flame. The residue in the bomb appeared caked a little but otherwise unchanged.

Test No. 3:

In this test the coal was made into a paste with some used lubricating oil and nickel chloride and iron oxide used as catalysts. The bomb was charged with hydrogen to a pressure of 1900 pounds. It was heated and the pressure was kept between 2800 pounds and 3000 pounds at a temperature of 310°-400° for four hours. The welding around the gauge pipe fitting sprung a leak and spoiled the test. At the leak a black tarry substance oozed out of the hole. It solidified at a higher temperature than tar but otherwise resembled it.

Test No. 4:

The bomb was fired at the Building and Repair department and charged as in test 3 for another trial. The initial hydrogen pressure was 1850 pounds and heat applied. The pressure was then held at 3000 pounds to 3500 pounds for four hours. The temperature was 350° to 370° C. The bomb was allowed to cool, and gas collected. When tested with fire it would pop and then burn for a while with a hot blue flame. It also gave a test for carbon dioxide with barium hydroxide. The residue in the bomb smelled strongly of coal tar products, but it appeared unchanged.

Test No. 5:

The bomb was recharged with coal paste and iron oxide, copper oxide, barium carbonate, antimony metal, and zinc dust were added for catalysts. Hydrogen pressure at the start was 1100 pounds and after heating for two hours it read 2500 pounds at a temperature of 340° C. The pressure was held at 2400 pounds to 2400 pounds for three hours. It was allowed to cool and pressure went down to 1070 pounds, and the gas was collected. It smelled of phenol or coal tar derivatives. More hydrogen was run into the bomb to a pressure of 1150 pounds and heated again. The pressure was held at 2400 pounds to 2300 pounds for two and one-half hours. The bomb seemed to leak a little. The bomb was allowed to cool again, and the gas collected. It smelled of coal tar derivatives this time and burned with a blue flame. The bomb was opened and the residue examined. It smelled of coal tar but appeared to be unchanged.

Test No. 6:

The bomb recharged as in No. 5 except nickel chloride was also used as a catalyst. It was charged with hydrogen to 1140 pounds and was heated up. The pressure never exceeded 1850 pounds. At this point it started leaking around the two pipe fittings which held the gauge and valve and also at the welding of the pipe opening.

Further work was impossible with the bomb.

CONCLUSION OF BOMB TESTS

In these tests the temperature and pressure desired was reached. A pressure of 2200 pounds to 2500 pounds was reached several times and a temperature of 325° to 400° C. The advantage of this over the pipe test was that in these tests larger quantities could be tested. In these tests one pound of coal was used for each run.

The disadvantages of this method were that the bomb had to be repaired or rewelded after every test or so, it was hard to handle, difficult to agitate properly, and whenever agitated the asbestos and cement insulation were often shaken loose.

These tests indicate that a catalyst was needed. They also indicate that the proper catalyst or correct combination of catalysts were not used. The catalysts recommended by the literature are metal oxides from the fourth to eighth groups.

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LITERATURE CITED

A New Gasoline.
Current History. April, 1927. Vol. 26:84.

Economic Problem of Liquefaction of Coal.
Power Plant Engineering. Dec., 1927. Vol. 31:1254.

Fluid Fuel From Coal.
Scientific American. July, 1927. Vol. 137:65-7.

Gasoline From Liquid Coal.
Literary Digest. Dec. 11, 1926. Vol. 91:21-2.

Hydrogenation of Coals in Presence of Catalysts.
Chemical Abstracts. June, 1929. Vol. 23:2806.

Light Oils From Utah Coal.
Power Plant Engineering. Oct., 1927. Vol. 31:1044.

Motor Fuels From Coal.
Automotive Industries. Nov. 25, 1926. Vol. 55:886-9.

Oil From Coal.
Quarterly Review. April, 1929. Vol. 252:249-58.

Riegel, E. R.
Introduction to Industrial Chemistry, pp. 304-5.

Synthetic Petroleum From Coal.
Scientific American. Jan., 1928. Vol. 138:72.

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